Page 12, line 26, change " $P > \dfrac{2\sqrt{3kTM}}{\tau} N_{ss}$ " to

$\beta 2$ -- $P > \dfrac{2\sqrt{3kTm}}{\tau} N_{ss}$ -- .

REMARKS

Applicants respectfully request entry of revised literal translation appended hereto.

I. CHANGES TO THE SUBSTITUTE SPECIFICATION

Claims 1-62 are pending. By this Supplemental Preliminary Amendment, the Substitute Specification is amended.

The changes are as follows:

A. On Page 1, line 37, "10 $cm^{-2} \cdot V^{-1} \cdot S^{-1}$ to 100 $cm^{-2} \cdot V^{-1} \cdot S^{-1}$" is changed to --10 $cm^2 \cdot V^{-1} \cdot S^{-1}$ to 100 $cm^2 \cdot V^{-1} \cdot S^{-1}$--. This change is necessitated by an inadvertent clerical error in the literal translation whereby "cm^{-2}" was inadvertently provided instead of "cm^2". This error is also been corrected in the attached revised literal translation.

B. On Page 2, line 5-6, "0.1 $cm^{-2} \cdot V^{-1} \cdot S^{-1}$ to 1 $cm^{-2} \cdot V^{-1} \cdot S^{-1}$" was changed to --0.1 $cm^2 \cdot V^{-1} \cdot S^{-1}$ to 1 $cm^2 \cdot V^{-1} \cdot S^{-1}$--. This change is necessitated by an inadvertent clerical error in the literal translation whereby "cm^{-2}" was inadvertently provided instead of "cm^2". This error is also been corrected in the attached revised literal translation.

C. On Page 12, line 12, the equation " $F = \dfrac{1}{6} CV = \dfrac{1}{\sqrt{3kTm}}$ " is changed to -- $F = \dfrac{1}{6} cv = \dfrac{1}{2} \dfrac{1}{\sqrt{3kTm}}$ --. This change is necessary to conform the substitute specification

with the literal translation. The "CV" is no longer capitalized and the "1/2" is added to the right side of the equation. This change conforms the Substitute Specification to the literal translation filed on September 30, 1997.

D. On page 12, line 26, the equation "$P > \dfrac{2\sqrt{3kTM}}{\tau} N_{SS}$"

is changed to $-- P > \dfrac{2\sqrt{3kTm}}{\tau} N_{SS} --$. This change corrects the inadvertent capitalized "M" and changes it to a small "m" in conformance with the literal translation filed on September 30, 1997.

II. <u>CHANGES TO THE LITERAL TRANSLATION</u>

A revised literal translation is attached as a substitute for the literal translation filed September 30, 1997. The revised literal translation includes the following revisions which correct typographical errors. The correction of these typographical errors does not raise new matter because the changes are supported by the corresponding Japanese language PCT Application, i.e., PCT/JP97/00213. The literal translation filed September 30 is amended as follows:

A. Page 2, line 14, same change as indicated in Section IA of this Supplemental Preliminary Amendment.

B. Page 2, lines 18-19, same change as indicated in Section IA of this Supplemental Preliminary Amendment.

C. Page 18, line 6, "(m-3)" should read "(m^{-3})".

D.   On page 18, line 9, line 1

$$F = \frac{1}{6} cv = \frac{1}{2} \frac{1}{\sqrt{3kTm}}$$

should read:

$$F = \frac{1}{6} cv = \frac{1}{2} \frac{1}{\sqrt{3kTm}} .$$

E.   On page 19,

$$P > \frac{2\sqrt{3kTm}}{\tau} N_{ss}$$

should read:

$$P > \frac{2\sqrt{3kTm}}{\tau} N_{ss} .$$

III. Conclusion

Applicants respectfully request entry of the above amendments to the Substitute Specification and entry of the attached revised literal translation. The amendments and changes to the literal translation correct clerical and typographical errors. No new matter has been introduced

because the changes are all supported by the Japanese language
PCT Application.

Respectfully submitted,

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~~SPECIFICATION~~

HIGH ENERGY SUPPLY APPARATUS, METHOD OF FORMING CRYSTALLINE FILM AND METHOD OF MANUFACTURING THIN FILM ELECTRONIC DEVICE

BACKGROUND OF THE INVENTION

1. ~~Technical Field~~ — Field of the Invention

The ~~present~~ invention relates to a high energy supply apparatus such as a laser irradiation apparatus ~~as a representative,~~ a method of forming a crystalline film by using the high energy supply device, and a method of manufacturing a thin film electronic device including a ~~comprising the~~ crystalline film formed by the method.

2. ~~Background Art~~ Description of Related Art

As ~~the~~ screen size and ~~resolution of a~~ resolution LCD liquid crystal display (LCD) increase, a ~~driving systems therefor is~~ driving systems are transferred from ~~a~~ simple matrix systems to ~~an~~ active matrix systems, thereby enabling the ~~display~~ display of large volumes of information. The active matrix systems ~~permits~~ enable LCD devices ~~having over several~~ to have more than hundreds of thousands of pixels. ~~and which include~~ These systems include ~~comprises a~~ a switching element, such as a thin film transistor (TFT), for each pixel. ~~As substrates for various types of LCD,~~ Transparent insulating substrates, such as a fused quartz plate, a glass plate, ~~and the like~~

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which enable transmission type displays are used as substrates for various types of LCD devices. A semiconductor film of amorphous silicon (a-Si) or polycrystalline silicon (poly-Si) is generally used to form an active layer for the TFT. When both the pixel switching element and the driving circuit are integrally formed by using a TFT, it is necessary and essential to use polycrystalline silicon exhibiting a high operation speed. When a polycrystalline silicon film is utilized as the active layer, the TFT is generally formed by using a fused quartz plate as a substrate in a manufacturing method referred to as a high-temperature process in which the maximum temperature exceeds 1000°C. In this case, the mobility of the polycrystalline silicon film is approximately 10 $cm^{-2} \cdot V^{-1} \cdot S^{-1}$ to 100 $cm^{-2} \cdot V^{-1} \cdot S^{-1}$. On the other hand, when an amorphous silicon is utilized to form the active layer, the highest temperature of the process is as low as approximately 400°C, and a glass substrate is thus generally used. The mobility of the amorphous silicon film is approximately 0.1 $cm^{-2} \cdot V^{-1} \cdot S^{-1}$ to 1 $cm^{-2} \cdot V^{-1} \cdot S^{-1}$.

Advances in enlargement of LCD display screens and reduction in cost require the use of a low-cost glass plate as an insulating substrate. However, as described above, amorphous silicon film is significantly inferior to polycrystalline silicon film in electrical

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properties, ~~and has problems of a~~ _and is subject to problems, such as having a_ low operation speed. ~~For example, etc.~~ On the other hand, the polycrystalline silicon TFT produced by the high temperature process ~~comprises~~ _includes_ a fused quartz plate, and thus ~~has the problems of causing~~ _is subject to the problems of increasing_ ~~difficulties in enlarging a~~ LCD ~~and reducing the~~ _increasing_ cost ~~thereof.~~ Therefore, there is strong demand for a technique for forming a thin film semiconductor device ~~comprising~~ _which includes_ a crystalline semiconductor film, such as a polycrystalline silicon film, ~~or the like~~ as an active layer formed on a usual glass substrate. In use of a _conventional_ ~~A usual~~ large glass substrate ~~having~~ _which has a_ high mass productivity, the highest temperature of the process is limited to ~~about~~ _approximately_ 400°C or less in order to avoid deformation of the substrate. This is referred to as a "low-temperature process poly-Si TFT" and _is_ now under development.

¶ ~~Eventually,~~ The most important technical problem _for development of a_ ~~of the~~ low-temperature process poly-Si TFT lies in ~~how to~~ form _ing an_ excellent crystalline film ~~by~~ _utilizing_ a processing temperature of 400°C or less, i.e., how to improve an apparatus for forming a good crystalline film. _Solving the aforementioned difficulties_ ~~Solution to such a problem~~ enables ~~not only the formation of~~ _development of_ a good TFT ~~and~~ _and_ LCD ~~comprising this TFT but~~ also significant improve _ments_ in _the_ performance of all electronic devices, such as solar cells and semiconductor device circuits, which are formed

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by using crystalline films. At the same time, this

~~enables a~~ *es* further reduction of the cost.

Conventionally, as
~~First prior art is~~ ^disclosed in SID (Society for

Information Display) '93 Digest P. 387 (1993), ~~in which~~ a

crystalline film is formed at a low temperature, and a

thin film electronic device ~~comprising~~ *including* the film is formed.

~~In this prior art,~~ *A* polycrystalline silicon film is

formed as the crystalline film, and a TFT is formed as the

thin film electronic device. The crystalline film is

formed by depositing an a-Si film of 50 nm by a low-

pressure chemical vapor phase deposition process (LPCVD

process) using monosilane (SiH$_4$) as a raw material at a

deposition temperature of 550°C, and then applying a laser

beam to the ~~thus~~ formed a-Si film. Although not disclosed

in this digest, irradiation of the laser beam is carried

out by the laser irradiation apparatus 101 shown in Fig.

1. The laser irradiation apparatus 101 ~~comprises~~ *includes* a laser

light emission source 102 and a laser irradiation chamber,

a substrate having a material 103 to be irradiated such as

the a-Si film which is placed on the surface thereof being

disposed on a stage 105 provided in the laser irradiation

chamber. In the laser irradiation chamber ~~is provided a~~ *is provided*

laser incident window ~~comprising~~ *which includes* quartz glass ~~or the like~~

at a position opposite to the stage so that a laser beam

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107 is incident through the laser incident window 106. The distance between the laser incident window and the substrate 104 is generally approximately 1 cm. The material to be irradiated is irradiated with a laser beam at a stage temperature from room temperature to about 400°C under pressure vacuum to atmospheric pressure.

After the poly-Si film including a crystalline film is obtained as described above, the thin film electronic device (TFT) is formed utilizing the poly-Si film. Specifically, after the poly-Si film is processed to a desired shape, an oxide film which functions as a gate insulating film is deposited by a PECVD process. A gate electrode is formed on the gate insulating film by using tantalum (Ta), and then a source and a drain for a transistor are formed, in a self alignment manner, by implanting donor or acceptor impurities into the polycrystalline silicon film using the gate electrode as a mask. Impurities are implanted by an ion doping method using a mass non-separation type implantation apparatus and phosphine (PH_3) and diborane (B_2H_6) as raw material gases which are diluted with hydrogen. The ions injected are activated at 300°C. The insulating layer is then deposited, and electrodes and wiring are formed by using indium tin oxide (ITO) and aluminum (Al) to complete a

TFT.

~~Second prior art~~ Another conventional method for obtaining a crystalline

semiconductor film at a low temperature is disclosed in

Japanese Patent Laid-Open No. 7-99321. ~~In this second~~

~~prior art,~~ A an a-Si film is formed and then irradiated with

a laser beam to obtain a crystalline film. Irradiation of

the laser beam is carried out under vacuum pressure ~~of vacuum~~ or

in an inert gas atmosphere. In fact, the same publication

discloses ~~in paragraph [0009]~~ the following. "At least

the surface layer of the semiconductor thin film formed on

the substrate is melted and recrystallized under reduced

pressure or in an inert gas atmosphere, and the substrate

(1) having the melted and recrystallized semiconductor

film formed thereon is transferred to the step of forming

an insulating film on the melted and recrystallized

semiconductor film while being maintained under reduced

pressure or in an inert gas atmosphere." ~~In the second~~

~~prior art,~~ A TFT is formed by a manufacturing method similar to the described above ~~basically the same as~~ the first ~~prior art~~ conventional method using the ~~thus~~

obtained polycrystalline silicon film. Eventually, in the conventional methods ~~both prior arts,~~ a crystalline film is obtained by

irradiating a silicon film with a laser beam using the

laser irradiation device shown in Fig. 2 under vacuum pressure ~~of~~

~~vacuum~~ to atmospheric pressure or in an inert gas

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atmosphere.

However, the above-mentioned ~~prior arts are considered as having~~ aforementioned convential~~ion~~ methods have the following problems:

~~Problem~~ (1) Irradiation under atmospheric pressure causes contamination of the crystalline film with impurities, such as oxygen and nitrogen or dust. Particularly, when the crystalline film ~~comprises~~ includes a semiconductor or a metal, contamination with oxygen or dust ~~brings about~~ creates significant deterioration in the physical properties of the thin film formed;

~~Problem~~ (2) The ~~A~~ gas frequently used in crystallization under an inert gas atmosphere is nitrogen. Since nitrogen ~~has~~ is highly ~~reactivity to~~ reactive with semiconductors such as silicon ~~and the like~~ and with ~~^~~ metals such as tantalum ~~and the like,~~ a high-purity crystalline semiconductor film and crystalline metallic film cannot be obtained;

~~Problem~~ (3) Irradiation under a ~~^~~ vacuum necessitates that a laser irradiation chamber with high sealing performance is provided, and a large scale evacuation device such as a turbo-molecular pump is added to a laser irradiation apparatus. This ~~brings about an~~ increases ~~in~~ the cost of a thin film electronic device ~~comprising~~ which includes a crystalline thin film, and ~~a~~ decreases ~~in~~ productivity;

~~Problem~~ (4) In melt crystallization, the component

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elements of the melted material irradiated with a laser

beam are invariably scattered or evaporated. This

phenomenon is particularly ~~remarkable~~ pronounced in laser irradiation

under vacuum because melting under a vacuum causes ~~the~~ the

formation of a deposited film. As a result, a film of the

material irradiated with a laser beam is formed on the

laser incident window of the laser irradiation apparatus.

Fig. 1 shows a scattered molecule 108 in this state.

Evaporation of the material 103 to be irradiated and the

formation of a film on the laser incident window represent

attenuation of the laser energy applied to the material to

be irradiated at each time of laser irradiation. Namely,

the ~~prior arts~~ conventional methods are incapable of obtaining a crystalline

film having good characteristics and ~~cause~~ instead possess large

variations in film quality;

~~Problem~~ (5) When high energy is supplied to the

material to be irradiated by laser irradiation ~~or the like~~

to progress melt crystallization, as the supplied energy

increases, the quality of the crystalline film ~~obtained~~ is

improved. However, in vacuum irradiation ~~under vacuum,~~ the problem described in

(4) above becomes significant as the supplied energy increases.

This makes it substantially ~~difficult~~ impossible to increase the

supplied energy ~~in~~ for vacuum irradiation ~~under vacuum~~ and improve

the quality of the crystalline film obtained; and

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~~Problem~~ (6) In laser irradiation under vacuum or in an

inert gas atmosphere, at the end of melt crystallization

by irradiation, *where* ~~at the time~~ the, material to be irradiated

with a laser beam is transferred from a solution state to

a crystal solid state, the surface is reconstructed to

minimize the surface energy, and many chemically active

unpaired bonding electrons remain on the surface. The

reconstructed surface having unpaired bonding electrons

has a structure completely different from that of the

internal crystal, and thus ~~shows~~ *exhibits* an energy band diagram

significantly ~~greatly~~ different from that of the internal crystal. ~~In~~ *Many electronic devices employ*

^ both ~~cases of a~~ semiconductor thin film and a metallic

thin film, *surfaces.* ~~many electronic devices employ the surfaces of~~

~~these films.~~ For example, ~~in a~~ field effect transistors

(FET) ~~comprising~~ *including* a semiconductor thin film, *where* an inversion

layer *is* formed on the surface of the semiconductor to

control the transfer process of electrons and holes in the

semiconductor. In metal wiring, of course, a current

flows through the surface of the metallic thin film. In a

device (for example, a mirror and a metal catalyst) which

employs the optical properties or chemical properties of a

thin film, the *device* characteristics ~~thereof~~ are determined by

the surface. *#* If the important surface having unpaired

bonding electrons is greatly different from the inside due

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to reconstruction, the physical properties of the surface

also greatly change (generally deteriorate). For example,

in a FET ~~comprising~~ that includes a semiconductor thin film, the

mobility in the inversion layer is decreased to several

tens to several % of the mobility of the inside of the

semiconductor according to the surface state. The same

phenomenon is observed in a metallic thin film (for

example, the electric conductivity of the metallic thin

film changes). As described above, control of the surface

plays an important part in obtaining a good crystalline

film. However, in a conventional crystallization method,

such control is not sufficiently ~~made~~ obtained, and thus ~~an~~ a

~~excellent~~ superior crystalline film cannot be obtained. Further,

the characteristics of the crystalline film (greatly) vary

with variations in the state of the reconstructed surface

at each ~~time of~~ melt crystallization.

Accordingly, the ~~present~~ object of the invention is ~~aimed at~~ to

solv~~ing~~e the above problems, and ~~an object material~~ therefor of the

~~invention is to~~ provide a high energy supply apparatus

such as a laser irradiation apparatus, ~~as a representative,~~

a method of forming a good crystalline film using the high

energy supply apparatus at a relatively low temperature,

and a method of manufacturing a thin film electronic

device ~~comprising~~ including forming the crystalline film formed by the

SUMMARY OF THE INVENTION

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disclosed
method.

~~Disclosure of the Invention~~

Summary of the Invention ✓ (CAP)

~~//////Control of atmosphere in melt crystallization)~~

In the ~~present~~ _first step of the_ invention, thin films of a
semiconductor ^_material_ such as silicon and a metal such as tantalum
are deposited on various substrates, ~~in a first step~~ and _in the_
second step at least the surface layers of these thin films are
partially melted and then crystallized through a cooling
solidification process _(hereinafter_ ~~(abbreviated to~~ "melt
crystallization" ~~hereinafter)~~ to form various crystalline
films, ~~in a subsequent second step.~~ Substrates to which
the ~~present~~ invention can be applied _and thin films are_ ~~will be~~ described _in_
detail ~~in Chapter (2-1), and the thin films will be~~ _hereafter below_
~~discussed in Chapter (2-2).~~ ~~The~~ Crystalline films ~~mean~~ _refer to_
films in a single crystal state, a polycrystal state or a
mixed crystal state wherein a crystal and an amorphous
material are mixed. Melt crystallization is achieved by
supplying high energy such as a laser beam to the thin
films. Possible forms of high energy include
electromagnetic waves such as light, X-rays, and gammer
rays ~~as representatives~~; charged particle flows such as

proton rays, electron rays, and alpha rays, and neutral elementary particle rays such as neutron rays and neutral meson rays. Elementary particle rays are advantageous because high energy can simply be supplied to the thin films through strong or weak interaction. Even when the thin films have low electric conductivity, neutral elementary particle flows containing electromagnetic waves (photon) do not apply unnecessary charges to the thin films and thus do not electrically damage the thin films during supply of high energy. This is particularly important when the thin films are intrinsic or nearly intrinsic semiconductor films, because these thin films have low electric conductivity. The charged particle flows have the advantage that they can easily be formed by generating a plasma of atoms, and that the directions of the charged particle flows can easily be controlled. In view of the ease of handling, including formation and direction control, and safety, the optimum high energy material is electromagnetic waves with a wavelength from about 10 nm to about 10 μm, i.e., light. Light can be classified into laser beams and nonlaser beams, both of which can be used as forms of high energy.

In the second step, metal crystallization proceeds in

~~a~~ *a mixed gaseous*

~~an~~ ^atmosphere containing ~~hydrogen such as a mixed gas containing~~ hydrogen molecules (H$_2$) and an inert gas; ~~a mixed gas containing~~ a hydrogen halide such as hydrogen fluoride (HF), hydrogen chloride (HCl) ~~or the like~~ and an inert gas; ~~a mixed gas containing~~ an inert gas and an acid such as nitric acid (NHO$_3$) *or* ~~,~~ sulfuric acid (H$_2$SO$_4$) ~~or the like;~~ ~~a mixed gas containing an~~ *or an* inert gas and a gas containing ~~as~~ a hydride of the component element of a thin film of a semiconductor ~~or the like~~, such as silane (SiH$_4$, Si$_2$H$_6$) ~~as a representative~~. As the inert gas, nitrogen (N$_2$), single rare gases such as helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) ~~and the like~~; mixed gases containing these gases, all gases chemically inert for thin films subjected to melt crystallization and mixed gases containing these gases ~~and the above inert gases~~ can be used.

~~Progress of~~ *M*elt crystallization of a thin film in an atmosphere containing an inert gas and hydrogen has the advantage*s* that it ~~is possible~~ to significantly decrease contamination of the thin film with impurities such as oxygen and dust particles floating in air$_\prime$ and improve the purity of the crystalline film formed$_\prime$ as compared with crystallization in atmosphere. For semiconductor films and metallic films, it is well known that as the amount

of ~~the~~ impurities in the film decreases, the physical

properties of the film such as mobility are improved. For

semiconductor films, impurities are intentionally added in

trace amounts of about 1 x 10^{18} cm^{-3} or less to control the

physical properties of the films. From this viewpoint,

~~also,~~ it is important to obtain a high-purity

semiconductor film. Contamination of the thin films from

air becomes more serious in melt crystallization than in

crystallization (solid phase crystallization or "SPC") in a

solid state. This is because in a liquid state where the

 processing temperature is higher than that in solid phase

crystallization, impurities diffuse and chemically react

with the components of the thin films at higher rates.

Therefore, control of the atmosphere in metal

crystallization ~~has more important meaning~~ is more critical than in solid

phase crystallization. ~~which follow~~ discussed below

It is important ~~from the viewpoints below~~ for reasons that the

atmosphere for progressing metal crystallization contains

hydrogen. When a thin film is melted by supplying high

energy and then solidified to a crystal, the adjacent

atoms in the thin film combine with each other to form a

regular crystal structure. However, on the upper half of the surface, no

bonding atoms ~~is~~ are present. ~~in the upper half thereof.~~ Hence,

in melt crystallization under vacuum or in an inert gas,

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~~on the surface of the thin film,~~ unpaired bonding
electrons combine with each other to reconstruct the
surface. /*on the surface of the thin film.*/ The structure of the reconstructed surface is
significantly ~~greatly~~ different from the inner structure of the crystal,
~~thereby~~ causing a change in the band structure. In
addition, large stress is present in the reconstructed
surface. This stress *causes* ~~affects as~~ lattice distortion *which affects the* ~~the~~
surface crystal *line film.* ~~positioned in an under layer up to several periods~~
~~thereof.~~ A change in the band structure changes the
concentrations of electrons and holes, and the lattice
distortion decreases the mobilit*y* ~~ies~~ of electrons and
holes. In addition, bonding of atoms on the surface
~~invariably~~ produces unpaired bonding electrons. These
electrons are chemically active and thus react with water
and oxygen in *the* air ~~or~~ *and also* absorb dust when the thin film is
exposed to air at the end of *the* crystallization *process.* ~~of the thin~~
~~film.~~ In addition, the presence of unpaired bonding
electrons produces interfacial levels and scattering
centers of electrons and holes, thereby deteriorating *the*
mobilit*y* ~~ies~~ of electrons and holes. Therefore, the
reconstructed surface ~~has various~~ adverse*ly* effects ~~on~~ the
physical properties of the thin films.

In the method of forming a crystalline film of the
~~present~~ invention, melt crystallization of the thin film

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proceeds in an atmosphere containing hydrogen. Therefore, the unpaired bonding electrons which appear on the thin film surface during the cooling solidification process are terminated by various types of hydrogen atoms (hereinafter "hydrogen·termination") contained in the atmosphere. The reconstruction of the surface is thus avoided, and at the same time, the total number of unpaired bonding electrons is significantly decreased. Therefore, the crystalline film obtained in accordance with the invention has high purity and a surface structure extremely close to the inner crystal line structure. As a result, the metallic surface simply reflects the intrinsic physical properties possessed by a metal itself, and the semiconductor surface also exhibits the physical properties of the semiconductor. For example, when a FET (so-called TFT) including a polycrystal semiconductor thin film is formed according to the present invention, because the mobility hardly deteriorates due to the reconstructed surface, the effective mobility is significantly improved, as compared to the effective mobility of a TFT formed by conventional techniques, the value mobility also does not change with substrates and lots.

Melt crystallization in a mixed gaseous atmosphere

mixed gas containing hydrogen molecules and an inert gas, does not introduce yet impurity into a crystallized film of a metal or semiconductor, and therefore, a high-purity crystallized film terminated with hydrogen is obtained. During melt crystallization of a semiconductor film of silicon an like under atmosphere containing a hydrogen halide and an inert gas, the crystallized semiconductor film is securely terminated with hydrogen because that the halide relatively easily reacts with the semiconductor film. This is particularly effective for metallic thin film. It is ideal for melt crystallization to progress in an mixed gaseous atmosphere containing an inert gas and a gas containing a hydride of the component of the thin film. This is because hydrogen termination occurs and high purity is guaranteed. For example when the thin film includes silicon, the best hydride is silane. Since silane rapidly reacts, it securely reacts with the unpaired bonding electrons which appear on the surface. This occurs because, as a result of reaction, even if silane is captured by the silicon thin film, only a silicon atomic layer is formed, without causing either a decrease in purity or lattice distortion.

In order to securely effect hydrogen termination in

melt crystallization, the ~~sufficient~~ partial pressure of

hydrogen or hydride in the atmosphere ~~is~~ ^should be^ about 10 mTorr or

more. This is based on the following reasons. If the

mass of one molecule of a gas is m (kg), the partial

pressure is P (Pa), the temperature is T (K), the

concentration is C (m-3) and the average velocity is v

(m·s⁻¹), ^then^ the flux density F (m⁻²·s⁻¹) of the gas is ~~as~~ ^represented by^

^the following equation^ ~~follows:~~ :

$$F = \frac{1}{6} cv = \frac{1}{2} \frac{1}{\sqrt{3kT/m}} \qquad \ldots (1) \text{ [Equation 1]}$$

wherein k is·the Boltzmann's constant. If the melting

time of recry^s^tallization is indicated by τ (s), and the

density of unpaired bonding electrons on the thin film

surface is indicated by Nss (m⁻²), in order to terminate

all unpaired bonding electrons, it is a necessary

condition that the number of gas molecules (flux density x

melting time) which collide with the thin film surface

within the melting time is larger than the density of

unpaired bonding electrons. Namely, the following

equation is established:

$$F \tau > Nss \qquad \ldots (2) \text{ [Equation 2]}$$

From Equations (1) and (2), the following equation is

obtained for pressure:

$$P > \frac{2\sqrt{3kTm}}{t\,\tau}\,Nss \qquad \ldots (3) \quad \text{[Equation 3]}$$

When the partial pressure of hydrogen atoms or hydride satisfies Equation 3, a high quality surface can be obtained after melt crystallization. The ~~possible~~ shortest possible time of melt crystallization is generally 10 ns ($\tau = 1 \times 10^{-8}$ s), and the maximum density of the unpaired bonding electrons, ~~which is conceivable in a practical manner,~~ is about 1×10^{12} cm^{-2} ($Nss = 1 \times 10^{16}$ m^{-2}). Therefore, if the partial pressure of hydrogen molecules or hydride is ~~hither~~ higher than the pressure calculated by using these values, Equation (3) is satisfied in melt crystallization of all thin films. The minimum partial pressure calculated for each hydride is as follows:

hydrogen molecule (H_2) $PH_2 > 1$ mTorr

hydrofluoric acid (HF) $PHF > 3$ m Torr

hydrochloric acid (HCl) $PHCl > 4$ mTorr

silane (SiH_4) $PSiH_4 > 4$ mTorr

nitric acid (HNO_3) $PHNO_3 > 6$ mTorr

sulfuric acid (H_2SO_4) $PH_2SO_4 > 7$ mTorr

Equation (3) indicates that the minimum partial pressure of a hydride increases as the molecular weight increases. However, the above results also indicate that ~~it is~~

almost all materials have a partial pressure of higher than about 10 mTorr. The lower limit concentration of hydrogen is about 4%, and the partial pressure of hydrogen corresponding to this value is about 30 Torr. From the viewpoint of safety, the maximum partial pressure of hydrogen is about 30 Torr. The lower limit concentration of silane is about 1%, and the partial pressure of silane corresponding to this value is about 7.6 Torr. From the viewpoint of safety, the other hydrides are preferably used at concentrations of about 1% or less, or partial pressure of about 7.6 Torr or less. With a margin for safety, the maximum partial pressure is about 5 Torr. Therefore, for all hydrides (including hydrogen molecules), the partial pressure of melt crystallization which for safely achieves the object of the present invention is 10 mTorr to 5 Torr.

Although the partial pressure of the hydride used in the second step has been described above, the total pressure is preferably atmospheric pressure or higher. Of course, melt crystallization under low pressure (vacuum) which satisfies the above partial pressure condition produces the same effect as described above. However, in a vacuum system apparatus, the cost is increased, and the process

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complicated. Melt crystallization under atmospheric
pressure simplifies the apparatus and the process, thereby
significantly improving productivity. Further, when
processing in the second step is carried out under
atmospheric pressure or higher, in metal crystallization,
it is possible to significantly decrease evaporation and
scattering of the component elements of the thin films and
adhesion of the evaporated and scattered elements in the
apparatus, as compared with processing under vacuum
(~~referred to as~~ *(hereinafter* "scattering suppression effect"
~~hereinafter~~). This is caused by the fact that the melted
surface is pressed by the gases which form the atmosphere,
and evaporation and scattering are suppressed in
proportion to pressure. Since the degree of this effect
is determined by the level of total pressure, in
principle, even if the pressure of only the hydrogen
molecules or hydride used is increased to atmospheric
pressure without using an inert gas, the same scattering
suppression effect as the use of a mixed gas containing a
hydride and an inert gas under atmospheric pressure can,
of course, be obtained. However, it is very dangerous to
handle such hydrides under atmospheric pressure. For this
reason (guarantee ~~for~~ *the* safety *of*), a mixed gas containing
hydrogen or hydride and an inert gas is preferable. As
advantage of low price. When a metal or semiconductor is

the inert gas, nitrogen is most widely used and has the advantage being inexpensive. When a metal or semiconductor is put into a high-temperature liquid state by supplying high energy, it reacts with nitrogen. However, rare gases have the advantage that they do not under any circumstances react with thin film materials, even at high temperatures. Materials utilized for thin films such as silicon and aluminum have relatively high atomic weights. Thus, of the rare gases, elements with high atomic weights, such as argon, krypton and xenon, have the larger scattering suppressing effect. Since krypton and xenon are not found in abundance, these elements are expensive. However, argon gas is inexpensive, practical and exhibits a large scattering suppression effect.

(1-2. Form of a high-energy supply apparatus and metal crystallization by the apparatus)

In the second step, high energy is supplied to an object material, such as the semiconductor thin film and metallic thin film formed on the substrate in the first step of the invention, to melt and crystallize at least the surface layer, and obtain a high-quality crystal, a high energy supply apparatus is required.

CAPS →

Detailed Description Of ~~the~~ PREFERRED EMBODIMENTS

The high energy supply apparatus is described ~~by~~ using light (laser beam) as an example of ~~the~~ a form of high energy, with reference to ~~Fig.~~ Figure 2. ~~At the same time,~~ The method of forming a crystalline film, using the thin film formed on the substrate in the first step of the invention as the object material to which high energy is supplied ~~in~~ during the second step, will be discussed.

The high energy supply apparatus shown in Figure 2, ~~(Fig. 2)~~ of the ~~present~~ invention ~~comprises~~ includes at least a generation source (laser emission source) 202 for generating high energy 207 such as a laser beam, and a supply chamber 201 in which the generated high energy is supplied to an object material (the substrate on which a thin film is formed). The supply chamber 201 has a function (setting base) 205 for setting the object material 203 in the supply chamber. The setting base 205 is provided with a movable function so that the high energy 207 can be supplied to a desired position of the object material. In a portion of the wall 209 of the supply chamber 201 is provided an introduction window 206 for introducing high energy 207 into the supply chamber. The introduction window 206 ~~comprising~~ includes a material which ~~less~~ little absorbs high energy and ~~hardly~~ transmits few gas molecules. In other words, the introduction window 206 is transparent to high energy 207 and opaque to gas molecules.

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For example, when the form of high energy is light, the introduction window includes ~~comprises~~ transparent glass such as quartz.~~or the like.~~

In the ~~present~~ invention, the introduction window 206 is provided at a position where, when high energy is supplied to the object material 203 (for example, a silicon thin film), the components (in the case of a silicon thin film, silicon atoms) of the object material 203 hardly adhere to the introduction window. For example, in the high energy supply apparatus, ~~shown in Fig. 2,~~ a portion of the wall of the supply chamber 201 is projected in a direction apart from the object material 203, and the introduction window 206 is provided at the top of the projected portion 210. As a result, the distance L1 between the introduction window 206 and the object material 203 is larger than the shortest distance L2 between the wall 209 and the object material 203.

In a state where~~in~~ the distance between the introduction window 206 and. ~~the~~ thin film as the object material is larger than the shortest distance between the wall 209 and the thin film, i.e., in a state wherein the introduction window 206 is provided at a position where the components of the thin film hardly adheres to the introduction window 206 even by supplying high energy 207 to the thin film, the high energy 207 is supplied to the thin film as the object material 203.

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In Fig. 2, the scattering range of the elements evaporated and scattered from the object material 203 as a result of supply of high energy 204 (irradiation of a laser beam) is shown as the scattered component. In the invention, since the introduction window 206 is sufficiently separated from the object material 203, as compared with the scattering range of the object material 203, the components of the object material 203 hardly adhere to the introduction window 206 even if melt crystallization by supplying high energy 207 is repeated. As described above, the introduction window 206 must be transparent to high energy. Since the object material 203 is opaque to high energy, high energy is converted into heat. If the object material 203 adheres to the introduction window 206, the introduction window becomes opaque and thus does not have the function to fulfil. In the invention, a high energy supply apparatus having excellent stability and productivity is realized.

When a crystallized film is obtained by irradiating the semiconductor thin film with a laser beam, it is particularly important to control the scattering range. Generally, the higher the energy supplied to the semiconductor thin film, the easier a good crystallized film is obtained. However, if the supplied

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energy exceeds a certain upper limit, the semiconductor

elements are explosively scattered, resulting in the

absence of the semiconductor thin film or a decrease in

the thickness thereof after supply of high energy. This

is possibly caused by the fact that the semiconductor film

includes a covalently bonded crystal and is hard and has

lower thermal conductivity than that of metals. Another

possible cause is that since the semiconductor thin film

is deposited by the vapor phase deposition process (CVD

process) in the first step, the adhesion between the

semiconductor film and the substrate or a surface

protective film formed on the substrate is low. In

either case, since the upper limit is present, the energy

of the laser beam supplied for performing crystallization

is set to as a high value as possible, which is lower than

the upper limit. However, the energy of the laser beam

invariably changes, and the explosive scattering occurs in

a statistical process. Therefore, in order to obtain a

good crystalline semiconductor film, the scattering

phenomenon cannot necessarily be ignored. From the above

situation, it can be concluded that the high energy supply

apparatus and the crystallized film forming method of the

present invention, in which the scattering range is

controlled, are particularly suitable for stably forming a

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good crystalline semiconductor film on the substrate or

the surface protective film with high productivity.

In order to decrease the size of the high energy

supply apparatus and facilitate replacement of the

atmosphere in the supply chamber, the unnecessary space in

the supply chamber must be eliminated as much as possible.

In consideration of setting and removal of the object

material 203 and vibration in the operation of the setting base 205,

the shortest distance between the wall and the object

material 203 is approximately 2 mm to 40 mm. On the other hand, the

scattering range of the object material 203 changes with

pressure in the supply chamber. For example, the

scattering range under a vacuum of about 10^{-5} Torr reaches

approximately 10 cm or more, while the scattering range under

atmospheric pressure is approximately 10 mm or less. Therefore,

if melt crystallization is progressed under pressure of

atmospheric pressure or higher, as described above, the sufficient distance between the

introduction window 206 and the object material 203 is about 20 mm

or more. If high energy 207 is supplied under pressure of

about 10 mTorr or less, the distance is preferably at

least about 50 mm, and ideally 100 mm or more. From these

viewpoints, in order to comply with various pressures in

the supply chamber 201, the distance is preferably about 50 mm

or more. Although there is no upper limit of this distance, if the upper limit is positively set, the upper limit is about 1000 mm. If the distance is too long, the volume of the supply chamber is increased, a lot of time is required for replacing the atmosphere, and the size of the apparatus itself is also increased.

(1-3. Gas flows in the high energy supply apparatus and melt crystallization performed thereby)

In the previous chapter, The optimum form of the high energy supply apparatus is described above. In this chapter, The gas flows in the supply chamber of the high energy supply apparatus will be described with reference to Figure Fig. 3.

Fig. 3(A) shows the structure of the supply chamber of the high energy supply apparatus described in the previous chapter from the viewpoint of the gas flows, and Fig. 3(B) shows gas flows 320 in the middle of crystallization of the object material performed by at least supplying high energy to the object material (the thin film formed on the substrate). The high energy supply apparatus of the invention includes pressure regulating means for generating a desired pressure distribution in the supply chamber 301, or gas flow regulating means for

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generating desired gas flows in the supply chamber. *301*

referring to Figure 3(A),

Specifically, ^the pressure regulating means or the gas

flow regulating means ~~comprises~~ *includes* at least an exhaust port

311 and a gas inflow port 312. The exhaust port is

provided at a portion of the wall 309 of the supply

chamber, for exhausting the air in the supply chamber. A

plurality of gas inflow ports (at the 6 positions shown in

Fig. 3(A)) are provided for flowing the various gases

described in detail *earlier* ~~in Chapter (1-1)~~ in the supply

chamber. The amount of the gas flowing through each of

the gas inflow ports and the exhaust rate of the exhaust

port are appropriately adjusted to control the total

pressure and flows in the supply chamber by the pressure

regulating means and the gas flow regulating means.

Additionally

~~Besides,~~ the pressure regulating means and the gas flow

regulating means are capable of increasing the pressure in

the vicinity of the introduction window 306 to a value

higher than that in the vicinity of the object material,

and increasing the pressure in the vicinity of the object

material to a value higher than that in the vicinity of

the exhaust port. Therefore, in the second step, the high

energy 307 is supplied to the object material ^*303* such as the

thin film set on the setting base 305 in the state wherein

the pressure in the vicinity of the introduction window is

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higher than that in the vicinity of the object material, ⟋*303*

or the pressure in the vicinity of the introduction window *306*

is higher than that in the vicinity of the object material *303*

(thin film) and the pressure in the vicinity of the object

material *303* (thin film) is higher than that in the vicinity

of the exhaust port.

The gas flows in this state will be described with

reference to Fig. 3(B). First, the path of the high

energy which is introduced into the supply chamber 301

through the introduction window 306 and then applied to

the object material 303 is assumed in the supply chamber.

Part of the high energy which reaches the object material

through the irradiation passage enters the object

material, and another part thereof is scattered and

reflected from the object material. In this application, *at Figure*

3(A) the scattered reflected high energy is referred to as

"reflected energy" 313 ✗. The path of the reflected energy *313*

in the supply chamber is assumed as a reflection passage

as shown in Figure 3B.

314. ^ As described above, the pressure distribution and

gas flows 320 regulated by the pressure regulating means

and the gas flow regulating means, respectively, are

present in the supply chamber. *301* In the supply chamber ^of *301*

the high energy supply apparatus of the ~~present~~ invention,

the gas flows ^*320* can be controlled so that gases flow toward

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the object material from the introduction window in substantially the same direction as the irradiation passage /315, and flow from the object material in substantially the same direction as the reflection passage /314. This ~~is caused by the fact that~~ occurs because the pressure in the vicinity ~~317~~ 317 of the introduction window^is higher than that in the vicinity ~~318~~ 318^, and the pressure in the vicinity of the object material is higher than that in the vicinity ~~319~~ of the exhaust port /319. Eventually, high energy is supplied to the object material such as the thin film to progress melt crystallization in the state wherein the gases flow from the introduction window in substantially the same direction as the irradiation passage and flow from the object material in substantially the same direction as the reflection passage. ,

As described ~~in the previous~~ ,above ~~previously,~~ ~~by~~ chapter, in melt crystallization of a metal or semiconductor, the component elements of the metal or semiconductor are invariably evaporated. With supply of high energy, the component elements are scattered as a fine powder. In the high energy supply apparatus of the ~~present~~ invention, since ~~the~~ gas flow from the introduction window side to the object side is present, the probability that the

evaporated elements or scattered fine powder reach the introduction window is significantly decreased. Since ~~the~~ gas flow 310 from the object material to the exhaust port is present in substantially the same direction as the reflection passage ~~is also present~~, the evaporated elements or scattered fine powder are exhausted through the gas flow. This ~~fact~~ not only prevents adhesion to and contamination of the supply chamber but also significantly restricts re-adhesion of the evaporated elements or scattered fine powder to the object material. ~~Particularly,~~ This particularly, has an important meaning when a TFT or a super integrated circuit (LSI) is manufactured by using ~~the~~ crystallized thin film formed on the substrate. This is because the fine powder which readheres to the thin film causes deterioration ~~in~~ of precision ~~of fine~~ processing and results in electrical short circuits. Since the fine powder is chemically active and has high reactivity to the wall of the supply chamber, the fine powder possibly re-adheres to the object material such as the thin film after such chemical reaction, thereby deteriorating the purity of the thin film itself. The high energy supply apparatus and the crystalline film forming method of the present invention can completely remove these adverse effects, and stably produce a good crystal.

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~~(1-4. Utilization of reflected energy)~~

~~In this chapter,~~ The high energy supply apparatus of the ~~present~~ invention described _earlier_ ~~in detail in Chapter (1-2)~~ _described as is_ is further ~~improved and~~ a method of forming a crystalline film using the apparatus, ~~will be described.~~

Fig. 4 shows the structure of a supply chamber 401 of the high energy supply apparatus of the ~~present~~ invention. ~~As described in Chapter (1-2),~~ The high energy supply apparatus ~~comprises~~ _includes_ at least a generation source ~~(omitted in Fig. 4)~~ for generating high energy 407 and a supply chamber _401_ for supplying high energy _407_ to an object material 403 (a metallic thin film or a semiconductor thin film). In the supply chamber _401_ is provided setting means 405 having the function to set the object material _403_ in the _supply_ chamber _401_. The object material _403,_ such as a substrate having a thin film _of the invention_ formed in the first step, ~~being~~ _is_ set on the setting means. In a portion of the wall 409 of the supply chamber _401_ ~~is~~ _is provided_ ~~provided~~ an introduction window _406_ for introducing high energy _407_ into the supply chamber _401_ so that the positional relationship between the introduction window 406 and the object material _403_ satisfies the conditions described ~~in~~ _above_ ~~Chapter (1-2).~~ In the supply chamber _401_ ~~are provided~~ pressure regulating means and gas flow regulating means _are provided which include_ ~~comprising~~ an exhaust port 411 and gas inflow ports 312,

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respectively, so that the pressure distribution and gas flows described ~~in Chapter (1-3)~~ earlier are present in the supply chamber/ 401. Of course, the atmosphere in the supply chamber 401 is set according to the description ~~in Chapter (1-1)~~ discussed earlier. The path of the high energy ∧ 407 introduced into the supply chamber 401 through the introduction window ∧ 406 and then applied to the object material ∧ 403 ~~assumed as~~ the irradiation passage ∧ 415.

In the high energy supply apparatus of the ~~present~~ invention, the introduction window ∧ 406 or the setting means ∧ 405 is disposed so that ∧ the direction of (416 line the normal ∧ of the object material ∧ 403 such as the thin film is shifted from the direction of the irradiation passage 415. Therefore, in crystallization of the thin film, high energy ∧ 407 is supplied to the thin film in the state wherein the normal direction ∧ 416 of the normal line of the thin film is deviated from the direction of the irradiation passage. / 415

In the high energy supply apparatus of the ~~present~~ invention, an exhaust port ∧ 411 is also provided in the normal direction ∧ 416 of the object material such as the thin film. Such a configuration permits an increase in the distance between the introduction window ∧ 406 and the object material ∧ 403 in the small supply chamber/ 401 and easily produces the same construction and effect described in Chapter (1-2). In addition, since the exhaust port ∧ 411 is provided at a position at the shortest distance between the object material ∧ 403 and

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the wall of the supply chamber 401, the evaporated elements

and scattered fine powder are effectively discharged.

Further, since the rate of discharge of the evaporated

elements and scattered fine powder in the normal direction 416

~~of the normal line~~ is particularly high, the efficiency of discharge is

improved, and the effect described ~~in Chapter~~ earlier (1-3) is

securely attained.

The high energy supply apparatus of the ~~present~~

invention ~~further comprises~~ also includes means for changing the course

of reflected energy so that the object material 403 ^is

irradiated again with the reflected energy 413. The

course changing means 418 further ~~comprises~~ includes positioning

means for permitting a desired position of the object

material 403 ^such as the thin film to be irradiated with the

reflected energy 413. After the thin film formed on the

substrate in the first step is set in the supply chamber 401,

a first position of the thin film is irradiated with high

energy 407. Part of the high energy 407 ^enters the thin film, and

another part is reflected from the thin film to generate

reflected energy. The course of the reflected energy 413 ^is

changed by the course changing means so that a second

position of the thin film is again irradiated to progress

melt crystallization. If the high energy 407 ^has a high

velocity, as light, irradiation of the second position is

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generally started with the reflected energy corresponding to the high energy for irradiating the first position of the thin film during the time of irradiation of the first position of the thin film with the high energy. The first position and the second position are adjusted by the positioning means 417. If the high energy 407 is light, the course changing means comprises an optical device such as a mirror, a lens or a prism. If the high energy is charged particles, the course changing means comprises an electromagnetic generator. The positioning function 417 is the function to change the positional relation (for example, the angle of the mirror) of an optical device, or finely adjust an electromagnetic field.

Figure 5 shows the simplest apparatus using light as high energy where Reference numeral 506 is an introduction window, 511 is an exhaust port, 512 is a gas inflow port and 516 is a normal line. Course changing means 518 includes a mirror, preferably converging means such as a concave mirror. Although reflected light generally contains scattered components, the converging means converges scattered light to permit efficient re-irradiation. Incident light is applied to the object material 503 such as the thin film

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and is then partially reflected to generate reflected

light. *513* The reflected light *573* is converged and reflected by

the concave mirror, and then applied to the object

material *503* again. This can significantly increase the

efficiency of utilization of the high energy 507. For

example, reflectance of ultraviolet light and visible

light by a semiconductor thin film reaches about 70% or

more, and the reflectance by a metal thin film is about

90% or more. Although a convention *al* efficiency of energy

utilization is ~~about~~ *approximately* 10% to 30%, the ~~present~~ invention can

substantially double the efficiency of energy utilization

from ~~about~~ *approximately* 20% to 50% because the reflected energy 513 is

efficiency re-utilized. This is particularly remarkable

when the irradiation position (first position) where the

object material is irradiated with high energy is

substantially the same as the irradiation position (second

position) where the object material is irradiated with the

reflected energy. *6* ~~In Fig. 6,~~ This effect is described

with reference to an example in which a laser beam is

emitted as pulses *and is illustrated in Figure 6*. In Fig. 6, the time at the non-

irradiation point of the object material is shown on the

abscissa, and irradiation is started at t = 0. The

intensity of energy (arbitrary unit) which actually enters

the object material to contribute to melt crystallization

is shown on the ordinate /axis. When irradiation is started,
the energy intensity of the high energy is increased to
the maximum at $t = t_1$. The reflected energy is applied to
the object material with a slight delay corresponding to
the distance between the object material and the course
changing means and the velocity. It is assumed that the
time the energy density of the reflected energy is the
maximum is t_2, the delay is indicated by $t_2 - t_1$. In this
way, the energy density of the incident high energy is
superimposed on the energy density of the reflected
energy. ~~In this application~~ This total of energy density
actually contributes to melt crystallization. ~~Fig.~~ Figure 6
shows this effect as synthetic light. As described above,
the ~~present~~ invention can substantially double the
conventional efficiency of energy utilization.

In the ~~further improved~~ high energy supply apparatus
of the ~~present~~ invention, the course changing means has
the function ~~to~~ of adjusting time. This function ~~is to~~ delays
the time (shown by $t2 - t_1$ in Fig. 6) of re-irradiation of
the object material with the reflected energy. (~~In this~~
~~application, the delay is referred to as~~ hereinafter "the delay time").
~~hereinafter).~~ For example, the time regulating means 419 in Figure

4 can be composed of a plurality of reflecting means which
can reflect the high energy. ~~Fig.~~ Figure 4 shows a simple

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example of this means. If the high energy is light, the

reflecting means is composed of combination of mirrors.

The time regulating means _419_ is means for changing the length

of the course of the reflected energy _413_ or changing the

velocity of the reflected energy _413_. The former means is

useful when the high energy is light, and the latter means

is useful when the high energy is charged particles. This

is because the course length of light can be changed by

changing combination of mirrors, and the velocity of

charged particles can be changed by adjusting an electric

field. The irradiation time of the object material with

high energy can be increased by appropriately adjusting

the delay time. This will be described below with

reference to Figure 7. #In Fig. 7, the same things as those

shown in Fig. 6 are respectively shown on the abscissa and

the ordinate. In Fig. 7, the delay time $(t_2 - t_1)$ is

substantially the same as the emission time width (the

half width of incident light shown by t_a in Fig. 7) of the

high energy. As a result, the half width of the synthetic

light is substantially doubled (shown by t_b in Fig. 7).

An increase in the time half width of the high energy

means that energy is rapidly supplied to the object

material, and the probability of occurrence of the

explosive scattering can significantly be decreased. For

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example, the hydrogenated amorphous silicon film (a-Si:H)
formed by a plasma chemical vapor phase deposition process
(PECVD process) is used as the object material, and the
object material is crystallized by irradiation with a
xenon·chlorine (XeCl) excimer laser (abbreviated to a XeCl
laser with a wavelength of 308 nm) as high energy. This
thin film generally has a high hydrogen content and a low
density, and is thus very difficult to melt crystallize.
In fact, an amorphous film is not at all crystallized by a
XeCl laser having a time half width of about 50 ns with an
irradiation energy density of about 100 mJ·cm^{-2} or less.
Conversely, if the energy density exceeds this value,
explosive scattering occurs. Eventually, the thin film is
not crystallized over the entire energy region. On the
other hand, the amorphous thin film is not crystallized by
a XeCl laser having a time half width of about 100 ns with
an irradiation energy density of about 100 mJ·cm^{-2} or less,
while with an energy density between about 100 mJ·cm^{-2} to
150 mJ·cm^{-2}, melt crystallization completely proceeds.
Although, with an energy density of about 150 mJ·cm^{-2} or
more, the explosive scattering occurs as described above,
the energy density range which enables melt
crystallization is widened by further increasing the time
half width. Even with the same energy density of 125

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$mJ \cdot cm^{-2}$, high energy having a short time half width (50 ns) and high energy having a long time half width (100 ns) have different effects on the object material. This difference is based on a difference in the energy transfer per unit time. With a long time half width, the amount of the energy transferred from high energy to the object material per unit time is decreased, thereby suppressing the explosive scattering. This is the same as a difference between combustion and explosion of an explosive. Explosion means the phenomenon which occurs when the energy transfer per unit time is large. For these reasons, in melt crystallization of an amorphous semiconductor film formed by PECVD or sputtering process at a relative low temperature (the substrate temperature is about 400°C or less) by supplying high energy, the time half width of the high energy is preferably about 100 ns or more. As described above, ~~in the present invention,~~ it is possible to simply increase the time half width, and crystallize the thin film which was conventionally considered as difficult to melt crystallize.

~~(1-5. Method of manufacturing thin film electronic device)~~

The high energy supply apparatus described in detail ~~in the~~ above ~~chapters~~, and the crystalline film formed by

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using the apparatus can be applied to various thin film
electronic devices~~, such as~~ *including* semiconductor devices such as
TFTs and LSIs, metal-insulator-metal elements (MIM
elements), solar cells, printed boards, etc., and the
performance ~~thereof~~ can significantly be improved. ~~In~~
~~this chapter, the~~ *A* method of manufacturing an excellent
thin film electronic device with reference to a TFT with
highest applicability as an example~~,~~ *is described.*

Figures A — D
Figs. 8(*A*) ~~to~~ (*D*) are schematic sectional views
showing the steps of manufacturing a thin film
semiconductor device (so-called TFT) which constitutes a
MIS type field effect transistor. The method of
manufacturing a TFT in accordance with the ~~present~~
invention will be briefly described.

The ~~present~~ invention uses general purpose non-alkali
glass as a~~n~~ *sample* ~~example of the~~ substrate. *In Figure 8(A),*
~~is formed~~ ^On a substrate 801 *is formed* a surface protective film 802 ~~comprising~~ *including* an
insulator by an atmospheric pressure chemical vapor
deposition process (APCVD process), t^*a*he PECVD process or
a the sputtering process, *or the like.* A semiconductor film, such as an
intrinsic silicon film serving as an active layer of a
thin film semiconductor device, is then deposited^*as the* ~~as~~ first
step for the semiconductor film~~)~~. The semiconductor film
is formed by a chemical vapor deposition process (CVD

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process) such as PECVD, APCVD or LPCVD or a physical vapor phase deposition process (PVD process), such as sputtering or vapor deposition. The ~~thus obtained~~ semiconductor film is supplied with high energy, such as a laser beam, for example, ~~as a representative~~ to progress melt crystallization for the second step for the semiconductor film). If the thin film deposited in the first step is amorphous or a mixed crystal containing an amorphous material and a fine crystal, the ~~this~~ second step is generally called "the crystallization step" On the other hand, if the thin film deposited in the first step is polycrystalline, the second ~~this~~ step is called the recrystallization step. ~~In the specification of this application.~~ No distinction is made between both cases, and this step is simply called the "crystallization step." Both cases correspond to the melt crystallization of this application as long as at least the surface of the thin film is melt crystallized by supplying high energy. Melt crystallization is an ~~extremity~~ excellent technique from the viewpoint that a high quality crystalline thin film can be formed on a large substrate with high productivity. In melt crystallization, by supplying high energy, the energy supply time (with a laser beam, the irradiation time) is generally as short as about 10 ns to 500 ns, and the

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energy supply region (laser irradiation region) is localized on the entire substrate. Thus, in crystallization, the entire substrate is not simultaneously heated to a high temperature, thereby causing no deformation or cracks due to the heat of the substrate. After the crystalline semiconductor film (polycrystalline silicon film) is formed according to the crystalline film forming method described above, the crystalline semiconductor film is processed to an island form, and an active semiconductor film 803 serving as an active layer of a transistor is formed.

After the active semiconductor film is formed, a gate insulating film 804 is formed by CVD or PVD (Fig. 8(b)). as illustrated in Figure 8(b). Referring to Figure 8(c), A metallic thin film serving as a gate electrode 805 is then deposited by PVD or CVD. Since the gate electrode and gate wiring are generally formed by using the same material in the same step, the material used must have low electric resistance and resist the highest temperature (in this example, about 350°C) and chemicals in the subsequent steps for manufacturing the thin film electronic device. Thus, a tantalum (Ta) film having such properties is formed by sputtering. The tantalum thin film formed by sputtering generally has a β-structure and resistivity of as high as about 200 $\mu\Omega$cm.

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The tantalum thin film also has internal stress and is apt to cause disconnection when used for wiring. In the invention, therefore, high energy is supplied to the tantalum thin film (a second step for the metal) to improve the quality of the thin film. When melt crystallization of the tantalum metallic thin film is progressed by the method described earlier, the crystallized film comprises α-structure tantalum (Ta). The α-structure tantalum has a cubic crystal system and a body-centered cubic crystal structure (bcc). The α-structure tantalum also has a resistivity of about 20 $\mu\Omega$cm to about 60 $\mu\Omega$cm and low internal stress. The α-structure tantalum is an excellent wiring material, as compared with the above β-structure tantalum.

After the metallic thin film which serves as the gate electrode and gate wiring is formed, shaping is carried out. Then, impurity ions are injected into the active semiconductor film to source-drain regions and channel formation region 806, 807 and 808, as illustrated in figure 8(C). At this time, since the gate electrode is used as a mask for ion injection, the channel formation region is formed only under the gate electrode in a self alignment manner. In order to inject impurity ions, two types methods can be used: an ion

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doping method for injecting hydride and hydrogen as impurity elements ~~to be~~ injected by using a mass non-separation ion injection apparatus; and an ion implantation method for injecting only a desired impurity element by using a mass separation type ion injection apparatus, ~~can be used.~~ When a CMOS TFT is formed, an appropriate mask material, such as polyimide resin, ~~or the like~~ is used, and NMOS and PMOS are alternately masked to inject each ion by using one of the above, methods described. Referring to Figure 8(D), ~~A Then~~, a layer insulating film 809 is then formed by CVD or PVD. After ion injection and formation of the layer insulating film, heat treatment is carried out for between several ~~tens~~ minutes to several hours in an appropriate heat environment of about 350°C or less to activate the injected ions and thermally shrink the layer insulating film. After the layer insulating film is formed, contact holes are formed above the source and drain, and a source-drain lead-out electrode 810 and wiring 811 are formed. At this time, the melt crystallization of the metallic thin film described earlier ~~in the previous chapters~~ may be applied to the metal which constitute the source-drain electrodes and wiring, as the gate electrode and gate wiring. After the crystalline metallic film is formed, the thin film is processed to electrodes and wiring to complete a thin film

semiconductor device (Fig. 8(d)).

~~(2-1. Substrate and surface protective film to which the present invention is applied)~~

~~In this chapter,~~ The substrate and the surface protective film ~~to which the present invention is applied will be described.~~ is newly described below. ~~As the~~ Substrate materials ~~to which the present~~ invention can be applied include conductive materials such as metals, ceramic materials such as silicon carbide (SiC), alumina (Al_2O_3), and aluminum nitride (AlN)~~, and the like~~; transparent insulating materials, such as fused quartz, and glass ~~and the like~~; semiconductor substrates including ~~such as~~ silicon wafers; and crystalline insulating materials, such as LSI obtained by processing semiconductor substrates, and sapphire (trigonal system Al_2O_3 crystal). ~~and the like can be used.~~ As an example of inexpensive ~~low-price~~ general purpose glass substrate, #7059 glass or #1737 glass produced by Corning Japan Co., Ltd., or OA-2 glass produced by Nippon Denki Glass Co., ltd., or NA35 glass produced by NH Technoglass Co., Ltd. ~~and the like~~ can be used. When a thin film semiconductor device is manufactured by using a crystalline semiconductor thin film, or when metallic wiring is formed by using a crystalline metallic thin film, at least a part of the substrate comprises an insulating material, and the

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crystalline thin film is formed on the insulating material regardless of the type of the substrate used. ~~In this application,~~ The insulating material film is hereinafter referred to as "the surface protective film". For example, when a fused quartz substrate is used, since the substrate itself includes ~~comprises~~ an insulating material, a crystalline film may be formed directly on the fused quartz substrate. Alternatively, the crystalline thin film may be formed after an insulating material such as a silicon oxide film $(SiO_x: 0 < x \le 2)$ or a silicon nitride film $(Si_3N_x: 0 < x \le 4)$ is formed as the surface protective film on the fused quartz substrate. When a glass plate is used as the substrate, generally, a crystalline film such as a semiconductor film may be formed directly on the glass substrate including ~~comprising~~ an insulating material. However, in order to prevent contamination of the thin film with movable ions such as sodium (Na) contained in glass, the crystalline film is preferably formed after the surface protective film is formed on the glass substrate by using an insulating material such as silicon oxide or silicon nitride. The thin film electronic device, such as the thin film semiconductor device manufactured as described ~~above~~ earlier, has ~~causes~~ no variation in operational characteristics in use for a long time or under a high voltage, thereby improving

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stability. In the case of the crystalline semiconductor film, the thin film is preferably formed on the surface protective film, except the case where a crystalline insulating material such as sapphire is used as the substrate. When any one of various ceramic substrates is used as the substrate, the surface protective film is preferably provided for preventing a sintering auxiliary material added to ceramic from diffusing into the thin film and contaminating it. When a metallic material is used as the substrate, the surface protective film is necessary and essential to secure insulating properties. In addition, in a semiconductor substrate and LSI device, the layer insulating film or the like provided between transistors or wiring layers plays a part as the surface protective film. The size and shape of the substrate are not at all limited as long as no deformation such as shrinkage, distortion or the like occurs in the heat environment of the manufacturing process. Namely, any desired substrate including a disk having a diameter of 3 inches *76.2 mm) and a rectangular substrate of about 600 mm x 800 mm or more can be used.

(2-2. Thin films to which the present invention can be applied, and gases containing the components thereof)

~~In this chapter,~~ The thin films to which the ~~present~~ invention is applied, and gases containing the component elements of semiconductor films among the gases which constitute the atmospheres described ~~in Chapter (1-1)~~ earlier are will ~~be~~ described below.

In the ~~present~~ invention, any kinds of crystalline materials can be used as the object material. For example, the ~~present~~ invention can be applied to melt crystallization of diamond. ~~or the like.~~ However, when a semiconductor thin film or a metallic thin film is selected as the object material, the advantageous effects of the ~~present~~ invention ~~is~~ are most simply and securely exhibited. The ~~present~~ invention can also be applied to all types of metals. Particularly, the ~~present~~ invention is effective for materials such as tantalum, described earlier ~~described in Chapter (1-5)~~ wherein the crystal phase is changed by supplying high energy or melt crystallization. Other metals in which the crystal grain size is increased as a result of metal crystallization are also preferred. Semiconductor thin films are most suitable for application of the ~~present~~ invention, because the semiconductor thin film formed in the first step is amorphous or crystalline with low quality, but ~~such~~ a low quality thin film is easily improved to an excellent crystalline thin film by

carrying out the second step of the invention.

The types of semiconductor films to which the invention can be applied include single semiconductor films of silicon (Si), and germanium (Ge); semiconductor films of Group IV element composite materials such as silicon·germanium (Si_xGe_{1-x}: $0 < x < 1$), silicon·carbide (Si_xC_{1-x}: $0 < x < 1$), and germanium·carbide (Ge_xC_{1-x}: $0 < x < 1$); semiconductor thin films of composite compounds of Group III elements and Group V elements such as gallium·arsenic (GaAs), and indium·antimony (InSb); and thin films of composite compounds of Group II elements and Group VI elements such as cadmium·selenium (CdSe). The invention can also be applied to semiconductor thin films of composite compounds such as silicon·germanium·gallium·arsenic (SixGeyGazAsz: $x + y + z = 1$); N type semiconductor films obtained by adding a donor element, such as phosphorus (P), or arsenic (As), antimony (Sb) to these semiconductor films; and P-type semiconductor films obtained by adding an acceptor element such as boron (B), aluminum (Al), gallium (Ga), indium (In) to these semiconductor films.

When the semiconductor film includes silicon (Si),

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gases containing the component element of the
semiconductor film include silanes, such as monosilane
(SiH$_4$), disilane (Si$_2$H$_6$), trisilane (Si$_3$H$_8$), and dichlorosilane
(SiH$_2$Cl$_2$), ~~and the like~~. When the semiconductor film
includes ~~comprises~~ germanium, germane (GeH$_4$) is used. When the
semiconductor film includes ~~comprises~~ phosphorus (P) or boron (B),
or when such an element is added to an intrinsic
semiconductor film, phosphine (PH$_3$), and or diborane (B$_2$H$_6$) ~~and~~
~~the like~~ can also be used. Although chemical materials
containing the elements which ~~constitute~~ include the above various
semiconductor films are used as gases for forming the
atmosphere, because ~~since~~ these gases ~~necessarily~~ partially remain
in the semiconductor films, hydrides of the component
elements are preferably used. For example, chlorine (Cl)
~~variably~~ remains in a silicon film formed by using
dichlorosilane (SiH$_2$Cl$_2$), regardless of the amount of
chlorine, and thus residual chlorine causes deterioration
in transistor characteristics when the silicon film is
used for the active layer of a thin film semiconductor
device. Therefore, monosilane (SiH$_4$), which is a hydride of
the component element, is preferred, as compared with
dichlorisilane.

~~(2-3. Laser beam as high energy)~~

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Types of light sources, when a laser beam is used as high energy source is described below. The laser beam used in the invention is not limited, and various light sources are used in accordance with the object material used. A KrF excimer laser (wavelength 248 nm) and a XeCl excimer laser (wavelength 308 nm) are widely used in the industrial field because of stable emission of light. Also, a ArF excimer laser and a XeF excimer laser (wavelength 351 nm) can also be used as the excimer laser. A YAG laser, a carbon dioxide laser, a Ar main beam laser (wavelength 514.5 nm), a Ar sub-beam laser (wavelength 448 nm), a HeNe laser (wavelength 632.8 nm), a HeCd laser (wavelength 441.6 nm), and other various pigment lasers can also be used. When the object material is a semiconductor film which includes silicon as a main component, a XeF laser, an Ar main beam laser, Ar sub-beam laser, HeNe laser, and HeCd laser exhibit higher absorption coefficients in the amorphous component than that in the crystalline component. This means that in a system containing an amorphous component and a crystalline component, energy absorption of the amorphous component is higher than that of the crystalline component, and the temperature of the amorphous component easily rises. Namely, crystallization of the amorphous component more

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easily takes place than recrystallization of the crystalline component. As described above, in melt crystallization of the semiconductor film, as the energy supplied increases within the range which causes no damage to the semiconductor film, the quality of the crystallized film obtained is improved. If the temperature of the crystalline component more easily rises, the semiconductor film is damaged before the amorphous component is completely crystallized. In other words, the film is damaged before recrystallization is completed. The XeF laser, for example, does not cause damage to the film, and is therefore very suitable for melt crystallization of a silicon semiconductor film. It is therefore important to select a high energy source whereby the absorption coefficient of the object material before supply of high energy is higher than that of the crystalline object material after supply of high energy.

Since the KrF laser and XeC laser exhibit high absorption coefficients in a semiconductor film including silicon as a main component, these lasers are suitable for crystallization of thin films having a thickness of approximately 50 nm or less. The absorption coefficients of the XeF laser and HeCd laser are slightly lower than those of the KrF laser and XeCl laser, and thus the XeF laser and HeCd

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laser are suitable for crystallizing silicon semiconductor thin films having a thickness of about 50 nm to 1000 nm. Since the absorption coefficients of Ar main beam laser and Ar sub-beam layer and HeNe laser in semiconductor films are low, they are suitable for crystallizing semiconductor thin films having a thickness of about 1000 nm or more.

As described above, the ~~present~~ invention enables simple stable melt crystallization of the object material by supplying high energy thereto, and easy formation of high-quality crystalline films. Such crystalline thin films permit manufacture of excellent thin film electronic devices. Specifically, the ~~present~~ invention has the following effects:

~~Effect~~ (1) Since crystallization ~~is progressed~~ *progresses* under control of an atmosphere which can ~~easily~~ safely be replaced, ~~no impurity~~ *no impurities* such as oxygen, nitrogen or dust ~~is~~ *are* captured by the crystalline thin film. Particularly, when the crystalline film ~~comprises~~ *includes* a semiconductor or metal, high purity and high quality crystalline film can be obtained.

~~Effect~~ (2) It is possible to supply high energy under atmospheric pressure, and thus simplify the high energy supply apparatus. *This)* decreases the cost of a thin film

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electronic device comprising which includes ^the crystalline film, and increases productivity;

Effect (3) In melt crystallization, the component elements of the object material are necessarily scattered or evaporated from the melted object material. It is possible to protect the incident window from evaporation, and thus keep the high energy supplied to the object material constant. A crystalline film having good characteristics can thus be obtained, and the quality of the film is significantly stabilized.

Effect (4) In progress of As melt crystallization progresses by supplying high energy, such as laser irradiation, to the object material, and ^as the energy supplied increases, the quality of the resultant crystal is generally improved. In this application, Since high energy can be applied under atmospheric pressure, even if the supplied energy is increased, the phenomenon such as scattering or evaporation can be suppressed, thereby improving the quality of the crystalline film.

Effect (5) Control of the surface plays an important role in obtaining a good crystalline film. In the crystallization method of the present invention, the control of the surface is sufficiently achieved, and thus an excellent crystalline film can be obtained. Further,

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since the recrystallized surface is controlled to the same state for each melt crystallization, the film characteristics are significantly stabilized.

(6) The efficiency of use of high energy can be substantially doubled. In addition, the time half width can be increased, and a material which cannot be crystallized by a conventional process can be crystallized.

These and other aspects and advantages of the invention will become apparent from the following detailed description of preferred embodiments when taken in conjunction with the accompanying drawings, in which:

Brief Description of the Drawings

Fig. 1 shows a conventional laser irradiation apparatus; Fig. 2 shows a high energy supply apparatus according to an embodiment of the invention; Fig. 3 shows a high energy supply apparatus of the invention; Fig. 4 shows a high energy supply apparatus according to an embodiment of the invention; Fig. 5 shows a high energy supply apparatus of the invention; Fig. 6 is a chart showing changes in the high energy supplied to an object material with time; Fig. 7 is a chart showing changes in the high energy supplied to an object material with time; Figs. 8(A) to (D) are sectional views showing the respective steps for manufacturing a thin film semiconductor device

in accordance with an embodiment of the ~~present~~ invention; # Figure shows ~~Fig. 9 is a drawing showing~~ the configuration of a

transmission type liquid crystal display device according

to the ~~present~~ invention; # Figure is a flowchart ~~Fig. 10 is a drawing~~ showing

the configuration of an electronic apparatus according to

the ~~present~~ invention; Figure shows a ~~Fig. 11 is a drawing showing an~~

~~example~~ liquid crystal projector utilizing an ~~of~~ electronic apparatus

according to the ~~present~~ invention; Figure shows ~~Fig. 12 is a drawing~~

~~showing~~ another example (personal computer) of an electronic

apparatus utilizing ~~according to~~ the present invention; and Figure ~~Fig. 13 is~~

shows ~~a drawing showing~~ a further example (pager) of an electronic

apparatus utilizing ~~according~~ to the ~~present~~ invention.

~~Best Mode for Carrying out the Invention~~

~~The present invention will be in further detail below~~

~~with reference to the drawings.~~

~~(Embodiment 1)~~
In another embodiment of the invention,
A surface protective film includes ~~comprising~~ a silicon oxide

film ~~is~~ formed on a large glass substrate of 360 mm x 475

mm x 1.1 mm by the PECVD process, and an intrinsic silicon

is
film ~~is then~~ formed on the surface protective film without
the This is deposition
breakage of the vacuum. This is the first step for silicon deposition. The

thickness of the surface protective film is 300 nm, and

the thickness of the semiconductor film is 60 nm. The

glass substrate in equilibrium with room temperature is set in an PECVD apparatus in which a lower plate electrode is kept at a temperature of 380°C. Conditions for depositing the silicon film are as follows:

Time: t = 164 s

Flow rate of silane: SiH_4 = 100 SCCM

Flow rate of argon : Ar = 3000 SCCM (raw material concentration 3.23%)

Power of radio frequency: RF = 600 W ($0.228W/cm^2$)

Pressure: P = 1.5 Torr

Electrode distance: S = 37.1 mm

Temperature of the under plate electrode: Tsus = 380°C.

Temperature of the substrate *is* surface: Tsub = 349°C The deposition rate of the semiconductor film under these conditions was 0.365 nm/s, and the thickness of the semiconductor film was 60 nm. The hydrogen concentration of the silicon film which was measured by thermal desorption gas spectroscopy (TDS) was 10.39 atomic %. Observation by a transmission electron microscope indicated that the silicon film mainly *includes* comprises a mixed crystal containing a prismatic structure amorphous component. The results of Raman spectroscopic measurement of the silicon film show *ed* a Raman shift at about 520 cm^{-1},

and thus indicates *d* that the silicon film of the ~~present~~ invention ~~comprises~~ *included* a mixed crystal.

The ~~thus obtained~~ silicon film was *then* irradiated with a laser beam to progress melt crystallization, {the second step for silicon}. Melt crystallization is carried out by a high energy supply apparatus having the laser irradiation chamber (supply chamber) shown in ~~Fig.~~ *Figure* 4. The laser beam is irradiated by using a KrF excimer laser having a wavelength of 248 nm and a half width of about 33 ns. Since reflected light is applied again with a delay time of about 30 ns by the time regulating means, the substantial time half width is about 60 ns. The time regulating means ~~comprises~~ *includes* a combination of mirrors, and the total length of the optical path of the reflected light is about 9 m. Incident light is applied at an angle of 60° with respect to the normal line. Since the shortest distance between the thin film and the wall of the supply chamber is 20 nm, the distance between the introduction window and the irradiation position on the thin film is generally 40 nm. The laser beam has a linear shape having a width of 120 μm and a length of 38 cm. The widthwise overlap of the beams applied in respective irradiations is 90% of the width of a beam. Therefore, a beam advances by 12 μm in each irradiation, and the same

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point on the semiconductor thin film is irradiated with a laser beam ten times. The energy density of the laser beam is 150 mJ·cm^{-2}. Irradiation of the laser beam is performed under atmospheric pressure. Mixed gases containing argon and monosilane are introduced into the supply chamber at a rate of 1 slm through the gas inflow port, and discharged through the exhaust port provided on the normal line of the thin film. The gases flows from the introduction window and the course changing means, including the positioning function and the time regulating means to the irradiation position, and further continues flow from the irradiation position toward the exhaust port. Since the silane concentration of argon is generally 100 ppm, the partial pressure of silane is generally about 76 mTorr in irradiation with the laser beam. In irradiation with the laser beam, the substrate temperature is at room temperature of about 25°C. The degree of crystallization of the crystallized semiconductor film, which was measured by multiwavelength dispersion type epsometory, was 98%, and the thickness was 55 nm. Raman spectroscopic measurement shows a sharp peak with a half width of 4.4 cm^{-1} at about 515 cm^{-1} which indicates a Raman shift caused by the crystalline component. This indicates that a high quality film having high

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crystallinity is formed. After the crystallization step, this crystalline film is patterned, and an active layer semiconductor film serving as an active layer of a transistor is then formed.

A gate insulating film is then formed by PECVD. The gate insulating film ~~comprising~~ _including_ a silicon oxide film is deposited to a thickness of 100 nm at a substrate surface temperature of 350°C by using TEOS $(Si-(O-CH_2-CH_3))_4)$, oxygen (O_2) and water (H_2O) as raw material gases and argon as a dilution gas. After the gate insulating film is formed, the oxide film is heat-treated in an atmosphere containing oxygen at a partial pressure of about 0.2 atm and water vapor with a dew point of about 80°C at a temperature of about 350°C for about 3 hours to improve the quality of the insulating film.

A tantalum (Ta) thin film serving as a gate electrode is then deposited by sputtering (the first step for tantalum). In sputtering, the substrate temperature is 150°C, and the thickness of the film is 500 nm. The ~~thus obtained~~ tantalum film is then irradiated with a laser (the second step for tantalum). Conditions for laser irradiation are the same as the conditions for crystallization of the semiconductor film except that the atmosphere gas is changed to mixed gases containing argon

and hydrogen. Since the hydrogen concentration of argon is about 1%, the partial pressure of hydrogen in laser irradiation is generally 7.6 Torr. The tantalum film after laser irradiation has the α structure, as described above, *earlier* and a resistivity of about 40 $\mu\Omega$cm. After the tantalum thin film ^*is formed* as the gate electrode, ~~is formed~~, pattering is performed.

An impurity ion is then injected into the semiconductor film to form source-drain regions and a channel region. At this time, the gate electrode served as a mask for injection, and the channel is formed only under the gate electrode in the self alignment manner. In this example, TFT having a CMOS structure is formed. The PMOS TFT portion is covered with a polyimide resin in formation of NMOS TFT source-drain, and conversely the NMOS TFT portion is covered with a polyimide resin in formation of PMOS TFT source-drain to form the CMOS TFT. An impurity ion is injected by using a mass non-separation type ion injection apparatus, and about 5% of phosphine (PH_3) diluted with hydrogen is used as a raw material gas for HMOS. The total of the ions including PH^{3+} and H_2^+ implanted is 1 x 10^{16} cm^{-2}, and the concentration of phosphorus atoms in the source-drain regions is about 3 x 10^{20} cm^{-2}. In ion injection, the substrate temperature is

250°C. For PMOS TFT, about 5% of diborane (B_2H_6) diluted with hydrogen is used as a raw material gas. The total of the ions including $B_2H_6^+$ and H_2^+ implanted is 1×10^{16} cm^{-2}, and the concentration of boron atoms in the source-drain regions is about 3×10^{20} cm^{-2}. In ion injection, the substrate temperature is also 250°C.

A layer insulating film ~~comprising~~ *including* a silicon oxide film is then formed by the PECVD process using TEOS. In deposition of the layer insulating film, the surface temperature of the substrate is 350°C, and the thickness of the film is 500 nm. Then heat treatment is performed at 350°C in an oxygen atmosphere for 1 hour to activate the injected ions and thermally shrink the layer insulating film. Contact holes are the formed on the source-drain, and aluminum (Al) is deposited by sputtering. In sputtering, the substrate temperature is 150°C, and the thickness of the Al film is 500 nm. The aluminum thin film for forming a source-drain lead out electrode and wiring is patterned to complete a thin film semiconductor device.

The transistor characteristics of the thin film semiconductor device formed on an experimental base were measured. The source-drain current Ids when the transistor is turned on at a source-drain voltage Vds of

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±4 V and a gate voltage Vgs of ±10 V is defined as an on current ION (+ and - signs of voltage indicate the measurement conditions of NMOS and PMOS, respectively). The source-drain current Ids when the transistor is turned off at Vds of ±4 V and Vgs of 0 V is defined as an off current. Measurement was carried out for a transistor in a channel formation region having a length L of 5 μm and a width W of 5 μm at a temperature of 25°C. Mobility and threshold voltage were calculated from the saturation current. In this embodiment, in order to examine the performance of the transistor and variations in the substrate thereof, measurement was made for 50 transistors uniformly formed on a large glass substrate. The results obtained are as follows:

NMOS TFT

ION = (74.3 + 9.0, -6.8) x 10^{-6} A

IOFF = (1.38 + 0.53, -0.37) x 10^{-12} A

μ = 124.1 ± 12.6 cm^2·V^{-1}·S^{-1}

Vth = 2.13 ± 0.13 V

PMOS TFT

ION = (51.6 + 4.7, -4.1) x 10^{-6} A

IOFF = (3.87 + 0.99, -0.80) x 10^{-13} A

μ = 69.3 ± 6.04 cm^2·V^{-1}·S^{-1}

Vth = -1.11 ± 0.11 V

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Therefore, the ~~present~~ invention is capable of
uniformly manufacturing a excellent CMOS thin film
semiconductor device with high mobility on a large
general-purpose glass substrate at ~~the~~ high~~est~~ *a* temperature
(350°C) ~~of the process as~~ the same as a conventional a-Si
which is   *temperature*
TFT. Since the TFT obtained in this example ~~comprises the~~ *a* *includes*
good crystalline semiconductor film and gate electrode,
~~the~~ reliability as a transistor is extremely high, and ~~the~~ *its* *its*
operation is stable over a long period of time. In a
conventional low-temperature process, uniformity of laser
crystallization is a very important problem regardless of
the substrates and lots. However, the ~~present~~ invention
can significantly decrease variations in the on-current
and off-current. This significant improvement in
uniformity means that the crystalline silicon film of the
~~present~~ invention has excellent properties, and
crystallization is stably progressed by the laser
irradiation apparatus (high energy supply apparatus) used.
In addition, since the tantalum film has low stress and
low resistivity, when the thin film semiconductor device
of the ~~present~~ invention is applied to LCD, uniform image
quality can be obtained over the entire LCD screen.
Further, when a circuit is formed by using the thin film
semiconductor device of the ~~present~~ invention, not only

simple circuits such as a shift register and an analog
switch but also complicated circuits such as a level
shifter, a digital analog converter circuit, a clock
generator circuit, a γ- correction circuit, and a timing
controller circuit can easily be formed.

~~(Embodiment 2)~~

In another embodiment of the invention,
An active matrix substrate containing the NMOS thin
film semiconductor device ~~obtained in Embodiment 1~~ *described above* and
used as a color LCD pixel switching element comprising 200
(line) x 320 (column) x 3 (color) = 192000 (pixels), the
CMOS thin film semiconductor device obtained ~~in Embodiment~~ *as described above*
and used as a 6-bit digital data driver (column
measurement driver) and a scanning driver (line
measurement driver) was manufactured. The digital driver
of this embodiment ~~comprises~~ *includes* a clock signal line, a clock
generator circuit, a shift register circuit, a NOR gate, a
digital image signal line, a latch circuit 1, a latch
pulse line, a latch circuit 2, a reset line 1, an AND
gate, a standard potential line, a reset line 2, a 6-bit
D/A converter based on volume division, a CMOS analog
switch , a common potential line, and a source line reset
transistor, the output from the CMOS analog switch being
connected to the source line of the pixel portion. The
volume of the D/A converter satisfies the relation of $C_0 =$

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$C_1/2 = C_2/4 = C_3/8 = C_4/16 = C_5/32$. ~~If~~ The digital image

signal line is directly input to the digital image signal

output from a video random access memory (VRAM) of a

computer. In the pixel portion of the active matrix

substrate of this embodiment, the source electrode and

source wiring, drain electrode (pixel electrode) ~~comprise~~ includes

aluminum to form a reflection type LCD. A liquid crystal

panel ~~comprising~~ including the ~~thus formed~~ active matrix substrate

as one of a pair of substrates is manufactured. A polymer

dispersion liquid crystal (PDLC) in which a black pigment

is dispersed is used as a liquid crystal held between the

pair of substrates to form a reflection type liquid

crystal panel in a normally black mode (a black display

when no voltage is applied to the liquid crystal). The

~~thus obtained~~ liquid crystal panel is connected to

external wiring to produce a liquid crystal display

device. As a result, the NMOS and PMOS have substantially

the same on resistance and transistor capacity, TFT has

high performance, and the parasitic capacity of the

transistor is very low. Further, since characteristics

are uniform over the entire surface of the substrates, the

6-bit digital data driver and the scanning driver are

normally operated over a wide operation range. Since the

pixel portion has a high degree of opening, even if black

pigment dispersion PDLC is used, a high quality liquid crystal display device can be obtained. Further, since the manufacturing process of the active matrix substrate is stable, the liquid crystal display device can stably manufactured at low cost.

This liquid crystal display device is contained in a casing of a full-color portable personal computer (note PC). The active matrix substrate contains the 6-bit digital data driver, and a digital video signal is input directly into the liquid crystal display device form the computer, the circuit configuration is simplified, and at the same time, power consumption is significantly decreased. Since the liquid crystal thin film semiconductor device has high performance, the note PC is a good electronic apparatus having a very beauty clear display screen. In addition, on the basis of the fact that the liquid crystal display device is a reflection type having a high degree of opening, a back light is made unnecessary, thereby realizing decreases in the size and weight of a batter and long-term use. As a result, a very small lightweight electronic apparatus which can be used for a long time and which has a beauty display screen could be formed.

Although an example using the reflection type active

matrix substrate had been described above, an embodiment

of the ~~present~~ invention can be applied to a liquid

crystal display device ~~comprising~~ *including* a transmission type

active matrix substrate. ~~Fig.~~ *Figure* 9 shows the entire

configuration of an example of such *a* liquid crystal display

device~~s~~. Namely, a liquid crystal display device

~~comprises~~ *includes* a back light 900, a polarizing plate 901, an

active matrix substrate 903 provided with a driving

circuit 902, a liquid crystal 904, a counter substrate 905

and a polarizing plate 906.

As illustrated in Figure 10, ~~An~~ An electronic apparatus ~~comprising~~ *including* the liquid crystal

display device of this embodiment ~~comprises~~ *includes* a display

information output source 1000, a display information

processing circuit 1002, a display driving circuit 1004, a

display panel 1006 such as a liquid crystal panel, a clock

generator circuit 1008 and a power source circuit 1010.

The display information output source 1000 ~~comprises~~ *includes*

memory such as ROM and RAM, and a tuning circuit for

tuning a television signal and outputting it so as to

output display information such as a video signal on the

basis of the clock generated from the clock generator

circuit 1008. The display information processing circuit

1002 outputs display information on the basis of the clock

generated from the clock generator circuit 1008, The

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display information processing circuit 1002 *includes* ~~comprises~~, for

example, an amplification-polarity inversion circuit, a

phase development circuit, a rotation circuit, a gammer

correction circuit or clamp circuit. The display driving

circuit 1004 *includes* ~~comprises~~ a scanning-side driving circuit and

a data-side driving circuit to drive the liquid crystal

panel 1006 to display an image. The power source circuit

1010 supplies electric power to each of the above

circuits.

Examples of electronic apparatus having the above-

described configuration include the liquid crystal

projector, shown in *Figure* Fig. 11, a personal computer (PC) for

multimedia and an engineering work station (EWS) shown in

Fig. ^*Figure* 12, the pager shown in *Figure* ~~Fig.~~ 13, a portable telephone,

a word processor, a television, a view finder type or

monitor direct-viewing type video tape recorder, an

electronic notebook, a table electronic computer, a car

navigation device, POS terminal, *and* a device with a touch

panel. ~~and the like.~~

The liquid crystal projector shown in *Figure* Fig. 11 is a

projection type projector ~~comprising~~ *which includes* a transmission type

liquid crystal panel as a light valve, for example,

employs a three-plate prism optical system.

In the projector 1100 shown in *Figure* Fig. 21, the

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projection light emitted from a white light source lamp unit 1102 is divided into the three primary colors R, G and B by a plurality of mirrors 1106 and two dichroic mirrors 1108 in a light guide 1104, and the three light parts are guided to three liquid crystal panels 1110R, 1110G and 1110B for respectively displaying images of the three colors. The light parts modulated by the liquid crystal panels 1110R, 1110G and 1110B are respectively incident on the dichroic prism 1112 in three directions. In the dichroic prism 1112, red light R and blue light B are bent at 90°, and green light straight travels to form an image of each color. As a result, a color image is projected on a screen through a projection lens 1114.

The personal computer 1200 shown in Fig. 12 Figure includes ~~comprises~~ a body part 1204 having a key board 1202, and a liquid crystal display screen 1206.

The pager ~~shown~~ 1300 in ~~Fig.~~ Figure 13 includes ~~comprises~~ a liquid crystal display substrate 1304, a liquid guide 1306 with a back light 1306a, a circuit substrate 1308, first and second shield plates 1310 and 1312, two elastic conductors 1313 and 1316, and a film carrier tape 1318, all of which are provided in a metallic frame. The two elastic conductors 1314 and 1316 and the film carrier tape 1318 are adapted for connecting the liquid crystal display

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substrate 1304 and the circuit substrate 1308.

In this apparatus, the liquid crystal display
substrate 1304 ~~comprises~~ *includes* a liquid crystal held between two
transparent substrates 1304a and 1304b to form at least a
dot matrix type liquid crystal display panel. On one of
the transparent substrates can be formed the driving
circuit 1004 shown in *Figure* Fig. 10 or the driving circuit 1004
and the display information processing circuit 1002.
Circuits which are not provided on the liquid crystal
display substrate 1304 can be provided as external
circuits of the liquid crystal display substrate on the
circuit substrate 1308 shown in ~~Fig.~~ *Figure* 13.

Figure ~~Fig.~~ 13 shows the configuration of the pager, and
thus the circuit substrate 1308 other ~~then~~ *than* the liquid
crystal display substrate 1304 is required. However, when
a liquid crystal display device is used as a component of
an electronic apparatus and when a display driving circuit
is mounted on a transparent substrate, the minimum unit of
the liquid crystal display device is the liquid crystal
display substrate 1304. Alternatively, the liquid crystal
display substrate 1304 fixed to the metallic frame 1302
serving as a casing can also be used as a liquid crystal
display device as a component of an electronic apparatus.
Further, in the case of a back light type, the liquid

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crystal display substrate 1304 and the light guide 1306 provided with the back light 1306a can be contained in the metallic frame 1302 to form a liquid crystal display device.

The ~~present~~ invention is not limited to the above embodiments, and various modifications can be made within the scope ~~of the gist~~ of the invention. For example, the ~~present~~ invention can be applied to not only the above-described various liquid crystal panels but also electroluminescence, plasma display devices.

~~Industrial Applicability~~

~~As described above,~~ The high energy supply apparatus of the ~~present~~ invention is also capable of stably producing high-quality crystallized films. The ~~thus obtained~~ crystalline films can be applied to thin film electronic apparatus such as thin film semiconductor devices, and significantly improve the performance thereof. The ~~present~~ invention can thus produce a thin film semiconductor device with high performance by using a low temperature process in which, for example, a low-price glass substrate can be used. When the ~~present~~ invention is applied to manufacture of an active matrix liquid crystal display device, a high quality large liquid

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crystal display device can easily and stably be manufactured. Further, when the ~~present~~ invention is applied to manufacture of an electronic circuit, a high quality electronic circuit can easily stably be manufactured.

The thin film semiconductor device of the ~~present~~ invention is low priced and has high performance, and is thus optimum as an active matrix substrate of an active matrix liquid crystal display device. Particularly, the thin film semiconductor device is optimum as an active matrix containing a driver required to have high performance.

A liquid crystal display device to which the ~~present~~ invention is applied is low priced and has high performance, and is thus optimum as various displays including a full-color note PC.

The thin film electronic apparatus of the ~~present~~ invention is ~~low priced~~ *inexpensive* and has high performance, and ~~will~~ *can* be ~~thus~~ widely used for general purposes.

ABSTRACT

The ~~present~~ invention ~~discloses~~ a high energy supply apparatus for stably producing a high quality melt crystallized film, and a method of forming a crystalline film ~~is shown~~. Melt crystallization is performed under control_{led} ~~of the~~ reconstruction of the surface of the crystallized film, without contaminating the high energy supply apparatus. In addition, ~~the efficiency of~~ ~~utilization of~~ high energy is efficiently utilized through ~~is increased by~~ reuse of reflected energy.